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**Langhoff, Boatz, Sheehy, Fajardo "Spectral Theory of Schroedinger Eigenstates: Theory and Applications for
Atomic Aggregates"**
HEDM Conference Presentation (Statement A)

**Spectral Theory of Schrödinger Eigenstates:
Theory and Applications for Atomic Aggregates^a**

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Progress is reported in the development and application of spectral methods for constructing the adiabatic electronic eigenstates and associated potential energy surfaces of metal-seeded cryogenic clusters relevant to the USAF HEDM Program.

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- ^a Supported in part by a grant from AFOSR to Indiana University.
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Outline of Remarks

Objectives & attributes of the spectral method:

- Eigenstates from a building-block approach; separation theorem for the many-body Hamiltonian; theoretical framework for analysis and applications

Review of the theory:

- Nature of the spectral-product basis; form of the Hamiltonian matrix; antisymmetry considerations; convergence to the physical subspace

Aspects of applications:

- Metal/rare-gas complexes; nonadditivity in ground-state structures; excited states in the presence of curve crossings; comparisons with cluster experiments; covalence and charge-transfer situations

Outlook & summary remarks:

Objectives and Attribute

- The primary objective is development of *ab initio* methods for calculations of the ground and excited adiabatic electronic eigenstates of large many-electron systems following an atomic building-block approach.
- Rigorously separates the many-body Hamiltonian into pair-interaction matrices which are obtained from quantities that can be calculated once and for all.
- Employs methodology devised for high-level molecular electronic structure computations, as well as a range of approximation methods.
- Provides a general framework for evaluations and comparisons of other atomic- and pair-based approximation schemes devised in various connections.

Theoretical Highlights

- The spectral product basis is complete but not overcomplete for calculations of antisymmetric states.
- The Hamiltonian matrix is pairwise-additive in interaction energy matrices which depend only upon the separations $R_{\alpha\beta}$ of the interacting atoms.
- Only atomic information $[\gamma^{(\alpha)}(r)]$ is required in construction of the pairwise-interaction matrices.
- One-electron transition density matrices $[\gamma^{(\alpha,\beta)}(r, r' : R_{\alpha\beta})]$ provide necessary and sufficient information for isolation of the totally antisymmetric subspace of the spectral product basis.

Review of the Theory

Hamiltonian Operator:

$$\hat{H}(\mathbf{1}, \mathbf{2}, \dots, \mathbf{n} : \mathbf{R}) = \sum_{\alpha=1}^N \left\{ \hat{H}^{(\alpha)}(\mathbf{i}) + \sum_{\beta=1}^N (\beta > \alpha) \hat{V}^{(\alpha, \beta)}(\mathbf{i}; \mathbf{j} : \mathbf{R}_{\alpha\beta}) \right\}$$

Spectral Product Basis:

$$\Phi(\mathbf{1}; \mathbf{2}; \dots, \mathbf{n} : \mathbf{R}) = \left\{ \Phi_a^{(1)}(\mathbf{1}) \otimes \Phi_a^{(2)}(\mathbf{2}) \otimes \dots \otimes \Phi_a^{(N)}(\mathbf{n}) \right\}_O$$

Hamiltonian Matrix:

$$\mathbf{H}(\mathbf{R}) = \sum_{\alpha=1}^N \left\{ \mathbf{H}^{(\alpha)} + \sum_{\beta=1}^N (\beta > \alpha) \mathbf{V}^{(\alpha, \beta)}(\mathbf{R}_{\alpha\beta}) \right\}$$

Atomic Terms:

$$\mathbf{H}^{(1)} = \left\{ \mathbf{E}_a^{(1)} \otimes \mathbf{I}_a^{(2)} \otimes \cdots \mathbf{I}_a^{(N)} \right\}_O$$

$$\mathbf{E}_a^{(1)} = \langle \Phi_a^{(1)}(\mathbf{1}) | \hat{H}^{(1)}(\mathbf{1}) | \Phi_a^{(1)}(\mathbf{1}) \rangle$$

Pairwise Interaction Terms:

$$\mathbf{V}^{(1,2)}(\mathbf{R}_{12}) = \left\{ \mathbf{v}^{(1,2)}(\mathbf{R}_{12}) \otimes \mathbf{I}_a^{(3)} \otimes \cdots \mathbf{I}_a^{(N)} \right\}_O$$

$$\mathbf{v}^{(1,2)}(\mathbf{R}_{12}) = \langle \Phi^{(1,2)}(\mathbf{1}; \mathbf{2}) | \hat{V}^{(1,2)}(\mathbf{1}; \mathbf{2} : \mathbf{R}_{12}) | \Phi^{(1,2)}(\mathbf{1}; \mathbf{2}) \rangle$$

Pair Product Basis:

$$\Phi^{(1,2)}(\mathbf{1}; \mathbf{2}) = \left\{ \Phi_a^{(1)}(\mathbf{1}) \otimes \Phi_a^{(2)}(\mathbf{2}) \right\}_{O_2}$$

$$\gamma_{n_1}^{(a)} \otimes \gamma_{n_2}^{(a)} = (1) \gamma_{n_1+n_2}^{(a)} + \sum_i (1) \gamma_{n_1+n_2}^{(i)}$$

The spectral product basis contains the totally antisymmetric representation of $S_{1+2+\dots n}$ once and only once, so that the associated matrix Schrödinger equation

$$H(\mathbf{R}) \cdot U(\mathbf{R}) = U(\mathbf{R}) \cdot E(\mathbf{R})$$

provides the physically correct solutions without linear dependence.

The prior antisymmetrized basis (Moffitt)

$$\Phi_a(1, 2, \dots, n; \mathbf{R}) = \hat{A} \left\{ \Phi_a^{(1)}(1) \otimes \Phi_a^{(2)}(2) \otimes \dots \otimes \Phi_a^{(N)}(n) \right\}_O$$

is linearly dependent in the limit of closure, so the associated Schrödinger equation

$$H_a(\mathbf{R}) \cdot U_a(\mathbf{R}) = S_a(\mathbf{R}) \cdot U_a(\mathbf{R}) \cdot E_a(\mathbf{R})$$

does not have unique solutions and is numerically unstable.

The Hamiltonian matrix

$$H_a(\mathbf{R}) = \langle \Phi_a(1, 2, \dots, n : \mathbf{R}) | \hat{H}(1, 2, \dots, n : \mathbf{R}) | \Phi_a(1, 2, \dots, n : \mathbf{R}) \rangle$$

is not pairwise additive in interaction matrices. It can be factored by noting that

$$\hat{H}(1, 2, \dots, n : \mathbf{R}) \Phi_a(1, 2, \dots, n : \mathbf{R}) = \hat{A} \hat{H}(1, 2, \dots, n : \mathbf{R}) \Phi(1; 2; \dots, n : \mathbf{R})$$

so that

$$H_a(\mathbf{R}) = S_a(\mathbf{R}) \cdot H(\mathbf{R})$$

The Schrödinger equation in the prior antisymmetrized basis becomes

$$S_a(\mathbf{R}) \cdot H(\mathbf{R}) \cdot U_a(\mathbf{R}) = S_a(\mathbf{R}) \cdot U_a(\mathbf{R}) \cdot E_a(\mathbf{R})$$

indicating that solutions of $H(\mathbf{R}) \cdot U(\mathbf{R}) = U(\mathbf{R}) \cdot E(\mathbf{R})$ provide the correct Schrödinger states employing post-antisymmetrization.

Reduction to the totally antisymmetric subspace:

$$\{\mathbf{v}^{(\alpha,\beta)}(R_{\alpha\beta})\} = \{\mathbf{v}^{(\alpha,\beta)}(R_{\alpha\beta})\}_a + \{\mathbf{v}^{(\alpha,\beta)}(R_{\alpha\beta})\}_r$$

Rotated interaction energy matrix:

$$\{\mathbf{v}^{(\alpha,\beta)}(R_{\alpha\beta})\}_a = \mathbf{D}^{(\alpha,\beta)\dagger} \cdot \mathbf{U}_a^{(\alpha,\beta)\dagger} \cdot \mathbf{E}_a^{(\alpha,\beta)}(R_{\alpha,\beta}) \cdot \mathbf{U}_a^{(\alpha,\beta)} \cdot \mathbf{D}^{(\alpha,\beta)} - \mathbf{E}_a^{(\alpha,\beta)}(\infty)$$

Construction of the transformation matrix:

$$\gamma_{\infty}^{(\alpha,\beta)}(\mathbf{r}, \mathbf{r}' : R_{\alpha\beta}) = \mathbf{U}_a^{(\alpha,\beta)}(R_{\alpha\beta})^{\dagger} \cdot \gamma^{(\alpha,\beta)}(\mathbf{r}, \mathbf{r}' : R_{\alpha\beta}) \cdot \mathbf{U}_a^{(\alpha,\beta)}(R_{\alpha\beta})$$

$$\gamma^{(\alpha,\beta)}(\mathbf{r}, \mathbf{r}' : R_{\alpha\beta}) = (n_{\alpha\beta}) \langle \Psi_a^{(\alpha,\beta)}(\mathbf{r}, 2, 3, \dots, n_{\alpha\beta}) | \Psi_a^{(\alpha,\beta)}(\mathbf{r}', 2, 3, \dots, n_{\alpha\beta}) \rangle$$

Conditions for the existence of the transformation (Friedman & Feshbach):

$$\int d\mathbf{r}' \gamma_{\infty}^{(\alpha, \beta)}(\mathbf{r}, \mathbf{r}' : R_{\alpha\beta}) \cdot \rho_i(\mathbf{r}') = \omega_i \rho_i(\mathbf{r})$$

$$\int d\mathbf{r}' \gamma^{(\alpha, \beta)}(\mathbf{r}, \mathbf{r}' : R_{\alpha\beta}) \cdot \rho_i(\mathbf{r}') = \omega_i \rho_i(\mathbf{r})$$

must provide unitary equivalent eigenvalues and eigenfunctions.

Electric dipole limit condition:

$$\mu_{\infty}^{(\alpha, \beta)}(R_{\alpha\beta}) = U_a^{(\alpha, \beta)}(R_{\alpha\beta})^{\dagger} \cdot \mu^{(\alpha, \beta)}(R_{\alpha\beta}) \cdot U_a^{(\alpha, \beta)}(R_{\alpha\beta})$$

$$\mu^{(\alpha, \beta)}(R_{\alpha\beta}) = \langle \Psi_a^{(\alpha, \beta)}(i, j) | \hat{\mu}(i, j) | \Psi_a^{(\alpha, \beta)}(i, j) \rangle$$

Solution:

$$U_a^{(\alpha, \beta)}(R_{\alpha\beta}) = U_d^{(\alpha, \beta)}(R_{\alpha\beta}) \cdot U_{\infty}^{(\alpha, \beta)}(R_{\alpha\beta})^{\dagger}$$

Aspects of Applications

Diatomic potential curves and transition moments:

NaAr - $^2\Sigma$, $^2\Pi$ & $^2\Delta$

AlAr - $^2\Sigma$, $^2\Pi$ & $^2\Delta$

LiH - $^1\Sigma$, $^3\Sigma$

Construction of the unitary transformation:

NaAr, AlAr - metal-rare-gas complexes

LiH - charge transfer

Cluster spectroscopy in curve-crossing situations:

AlAr₆, AlAr₁₂, AlAr₅₄ - $3p \rightarrow 3d, 4p$

Summary & Outlook

The theoretical development is largely but not entirely complete.

Applications to complexes have provided a useful vehicle for developing the method.

Applications to charge transfer and covalent diatomics illustrate requirements for more general bonding situations.

Calculations to date have employed ^(↑)existing high-level code suites without modification.

Stieltjes methodology can be implemented to provide the large spectral product sets required for a general applications package.

A program to address the issues associated with development of a general applications package is required.